

## 4.2 Fundamentals of Electron-Photon Interaction in Nanostructures<sup>1</sup>

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We describe the fundamental equations for description of electron-photon interactions in insulating nanostructures. Since the theory for the nanostructures are based on the theory for the bulk crystals, we shall describe elements of the theory for the bulk crystals [1]-[3] in the first three subsections. It is important in discussions on optical phenomena that *both* the envelope function and the Wannier functions (or, equivalently, cell-periodic parts of the Bloch functions) should be taken into account. The theory for the nanostructure is discussed in the fourth subsection. In the final subsection, we briefly mention quantum optics in nanostructures.

### 4.2.1 Electron and Hole Operators in Insulating Solids

To describe quantum states in solids, it is customary to start from a mean-field approximation to electrons in a perfect crystal. Then, according to the Bloch theorem, a single-body state of an electron in a solid crystal of volume  $V$  takes the following form:

$$\phi_{b\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} u_{b\mathbf{k}}(\mathbf{r}), \quad (4.2.1)$$

where  $b$  labels bands (conduction band, heavy-hole band, and so on), and  $u_{b\mathbf{k}}$  is the cell-periodic function which is periodic from cell to cell. The spin index is omitted for the sake of simplicity. The normalization is taken as

$$\int_V d^3r \phi_{b\mathbf{k}}^*(\mathbf{r}) \phi_{b'\mathbf{k}'}(\mathbf{r}) = \delta_{bb'} \delta_{\mathbf{k}\mathbf{k}'}, \quad (4.2.2)$$

$$\frac{1}{v_0} \int_{v_0} d^3\rho u_{b\mathbf{k}}^*(\rho) u_{b'\mathbf{k}}(\rho) = \delta_{bb'}, \quad (4.2.3)$$

where  $\rho$  denotes the coordinate vector in a unit cell, whose volume is  $v_0$ , and  $\int d^3\rho$  is over the unit cell.

We can construct the Wannier function which is localized around cell  $\ell$  as

$$w_b(\mathbf{r} - \mathbf{R}_\ell) \equiv \sqrt{\frac{v_0}{V}} \sum_{\mathbf{k}}' e^{-i\mathbf{k}\cdot\mathbf{R}_\ell} \phi_{b\mathbf{k}}(\mathbf{r}), \quad (4.2.4)$$

where  $\mathbf{R}_\ell$  is the center position of the cell, and  $\sum'$  denotes the summation over the first Brillouin zone. This function is normalized as

$$\int_V d^3r w_b^*(\mathbf{r} - \mathbf{R}_\ell) w_{b'}(\mathbf{r} - \mathbf{R}_{\ell'}) = \delta_{bb'} \delta_{\ell\ell'}, \quad (4.2.5)$$

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<sup>1</sup> A slightly shortened version has been published as section 4.2 of *Mesoscopic Physics and Electronics*, T. Ando et al. eds., Springer (1998), pp. 140-155.

and the inverse transformation is

$$\phi_{b\mathbf{k}}(\mathbf{r}) = \sqrt{\frac{v_0}{V}} \sum_{\ell} e^{i\mathbf{k} \cdot \mathbf{R}_{\ell}} w_b(\mathbf{r} - \mathbf{R}_{\ell}). \quad (4.2.6)$$

Note that both the Bloch functions and the Wannier functions form complete sets:

$$\sum_b \sum_{\mathbf{k}}' \phi_{b\mathbf{k}}^*(\mathbf{r}) \phi_{b\mathbf{k}}(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \quad (4.2.7)$$

$$\sum_b \sum_{\ell} w_b^*(\mathbf{r} - \mathbf{R}_{\ell}) w_{b'}(\mathbf{r}' - \mathbf{R}_{\ell}) = \delta(\mathbf{r} - \mathbf{r}'). \quad (4.2.8)$$

To describe many-body states, we introduce the electron field operator  $\hat{\psi}(\mathbf{r})$  which satisfies

$$\{\hat{\psi}(\mathbf{r}), \hat{\psi}^{\dagger}(\mathbf{r}')\} = \delta(\mathbf{r} - \mathbf{r}'), \quad \{\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')\} = 0. \quad (4.2.9)$$

We can expand  $\hat{\psi}(\mathbf{r})$  as

$$\hat{\psi}(\mathbf{r}) = \sum_b \sum_{\mathbf{k}}' \phi_{b\mathbf{k}}(\mathbf{r}) \hat{c}_{b\mathbf{k}} = \sum_b \sum_{\ell} w_b(\mathbf{r} - \mathbf{R}_{\ell}) \hat{c}_{b\ell}. \quad (4.2.10)$$

We can easily show that  $\hat{c}_{b\mathbf{k}}$  and  $\hat{c}_{b\ell}$  satisfy

$$\{\hat{c}_{b\mathbf{k}}, \hat{c}_{b'\mathbf{k}'}^{\dagger}\} = \delta_{bb'} \delta_{\mathbf{k}\mathbf{k}'}, \quad \{\hat{c}_{b\mathbf{k}}, \hat{c}_{b'\mathbf{k}'}\} = 0, \quad (4.2.11)$$

$$\{\hat{c}_{b\ell}, \hat{c}_{b'\ell'}^{\dagger}\} = \delta_{bb'} \delta_{\ell\ell'}, \quad \{\hat{c}_{b\ell}, \hat{c}_{b'\ell'}\} = 0, \quad (4.2.12)$$

and we can interpret  $\hat{c}_{b\mathbf{k}}^{\dagger}$  and  $\hat{c}_{b\ell}^{\dagger}$  as the creation operators of an electron whose wavefunction is  $\phi_{b\mathbf{k}}(\mathbf{r})$  and  $w_b(\mathbf{r} - \mathbf{R}_{\ell})$ , respectively.

We here consider a non-doped semiconductor or dielectric material. It is customary to define the creation operator of a hole by

$$\hat{h}_{v\mathbf{k}\uparrow}^{\dagger} \equiv \hat{c}_{v-\mathbf{k}\downarrow} \quad \text{when } v \text{ is a valence band,} \quad (4.2.13)$$

where only in this equation we recover the spin index for the reader's convenience. The ground state is the vacuum of the holes and the conduction electrons:

$$\hat{c}_{c\mathbf{k}}|g\rangle = \hat{h}_{v\mathbf{k}}|g\rangle = 0 \quad \text{for all } c, v \text{ and } \mathbf{k}, \quad (4.2.14)$$

where  $c$  and  $v$  stand for conduction and valence bands, respectively. We hereafter call a conduction electron simply an electron.

It is convenient to decompose the fundamental field  $\hat{\psi}$  into the electron and hole parts,  $\hat{\psi}_e$  and  $\hat{\psi}_h$ , respectively, as

$$\hat{\psi}(\mathbf{r}) = \hat{\psi}_e(\mathbf{r}) + \hat{\psi}_h^{\dagger}(\mathbf{r}), \quad (4.2.15)$$

$$\hat{\psi}_e(\mathbf{r}) \equiv \sum_c \sum_{\mathbf{k}}' \phi_{c\mathbf{k}}(\mathbf{r}) \hat{c}_{c\mathbf{k}}, \quad (4.2.16)$$

$$\hat{\psi}_h^\dagger(\mathbf{r}) \equiv \sum_v \sum_{\mathbf{k}}' \phi_{v\mathbf{k}}(\mathbf{r}) \hat{c}_{v\mathbf{k}} = \sum_v \sum_{\mathbf{k}}' \phi_{v\mathbf{k}}(\mathbf{r}) \hat{h}_{v-\mathbf{k}}^\dagger. \quad (4.2.17)$$

The anti-commutation relations are evaluated as

$$\{\hat{\psi}_e(\mathbf{r}), \hat{\psi}_e^\dagger(\mathbf{r}')\} = \sum_c \sum_{\mathbf{k}}' \phi_{c\mathbf{k}}(\mathbf{r}) \phi_{c\mathbf{k}}^*(\mathbf{r}') \equiv \delta_e(\mathbf{r} - \mathbf{r}') = \delta_e^*(\mathbf{r}' - \mathbf{r}), \quad (4.2.18)$$

$$\{\hat{\psi}_h(\mathbf{r}), \hat{\psi}_h^\dagger(\mathbf{r}')\} = \sum_v \sum_{\mathbf{k}}' \phi_{v\mathbf{k}}^*(\mathbf{r}) \phi_{v\mathbf{k}}(\mathbf{r}') \equiv \delta_h(\mathbf{r} - \mathbf{r}') = \delta_h^*(\mathbf{r}' - \mathbf{r}), \quad (4.2.19)$$

and other anti-commutators are zero. Note that

$$\delta(\mathbf{r} - \mathbf{r}') = \delta_e(\mathbf{r} - \mathbf{r}') + \delta_h^*(\mathbf{r} - \mathbf{r}'). \quad (4.2.20)$$

Hence,  $\delta_c$  and  $\delta_v$  work as projection operators onto subspaces which are spanned by  $\phi_{c\mathbf{k}}(\mathbf{r})$ 's and  $\phi_{v\mathbf{k}}(\mathbf{r})$ 's, respectively. *It is only in each subspace* that they work as delta functions and  $\hat{\psi}_e^\dagger(\mathbf{r})$  and  $\hat{\psi}_h^\dagger(\mathbf{r})$  can be interpreted as operators which create an electron and a hole, respectively, at the position  $\mathbf{r}$ . One should always keep this limited meaning of  $\delta_e$ ,  $\delta_h$ ,  $\hat{\psi}_e$  and  $\hat{\psi}_h$  in mind to avoid inconsistencies.

#### 4.2.2 Effective-Mass Approximation

A single-electron state can be obtained by operating  $\hat{c}_{c\mathbf{k}}^\dagger$  on  $|g\rangle$ . It is an eigenstate of the mean-field Hamiltonian  $\hat{\mathcal{H}}_{mf}$  of the perfect crystal:

$$\hat{\mathcal{H}}_{mf} \hat{c}_{c\mathbf{k}}^\dagger |g\rangle = \varepsilon_c(\mathbf{k}) \hat{c}_{c\mathbf{k}}^\dagger |g\rangle, \quad (4.2.21)$$

where we have taken  $\hat{\mathcal{H}}_{mf} |g\rangle = 0$ , and  $\varepsilon_c(\mathbf{k})$  is called the band energy. A single-hole state, on the other hand, is obtained by operating  $\hat{h}_{v\mathbf{k}}^\dagger$  on  $|g\rangle$ , and its energy is  $-\varepsilon_v(\mathbf{k})$ :

$$\hat{\mathcal{H}}_{mf} \hat{h}_{v\mathbf{k}}^\dagger |g\rangle = -\varepsilon_v(\mathbf{k}) \hat{h}_{v\mathbf{k}}^\dagger |g\rangle, \quad (4.2.22)$$

Suppose that  $\varepsilon_c(\mathbf{k})$  takes the minimum value at  $\mathbf{k} = \mathbf{k}_c$ , and  $\varepsilon_v(\mathbf{k})$  is maximum at  $\mathbf{k} = \mathbf{k}_v$ . The minimum energy cost for creating an electron in band  $c$  and a hole in band  $v$  is

$$\varepsilon_c(\mathbf{k}_c) - \varepsilon_v(\mathbf{k}_v) \equiv E_{Gcv}, \quad (4.2.23)$$

which is called the energy gap between bands  $c$  and  $v$ . In particular, the energy gap between the bottom (lowest) conduction band  $c_m$  and the top (highest) valence band  $v_m$  is simply called the energy gap, and is denoted by  $E_G$ . For simplicity, we hereafter assume that this gap is located at  $\mathbf{k} = \mathbf{0}$ , i.e.,  $\mathbf{k}_{c_m} = \mathbf{k}_{v_m} = \mathbf{0}$ :

$$\varepsilon_{c_m}(\mathbf{0}) - \varepsilon_{v_m}(\mathbf{0}) \equiv E_G. \quad (4.2.24)$$

We are interested in states with small  $k$  in bands  $c_m$  and  $v_m$ . We hereafter write  $c_m$  and  $v_m$  simply as  $c$  and  $v$ .

When an additional single-body potential  $V_1$ , which may be due to impurities, external potential, and so on, are present the additional term appears in the Hamiltonian;

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_{mf} + \int_V d^3r \hat{\psi}^\dagger(\mathbf{r}) V_1(\mathbf{r}) \hat{\psi}(\mathbf{r}) \equiv \hat{\mathcal{H}}_{mf} + \hat{\mathcal{H}}_1. \quad (4.2.25)$$

In this case,  $\hat{c}_{\mathbf{c}\mathbf{k}}^\dagger|g\rangle$ 's and  $\hat{h}_{v\mathbf{k}}^\dagger|g\rangle$ 's are no longer eigenstates, and we must take their linear combinations to obtain true eigenstates. The linear combination must be taken over different bands and different  $\mathbf{k}$ 's, in general. However, the band mixing may be negligible if (i) the spatial variation of  $V_1$  is slow (i.e., the characteristic length of the variation  $\gg$  lattice constants) and if (ii) the band of interest is well separated around  $\mathbf{k} = \mathbf{0}$  from other bands. (This condition is usually satisfied for the conduction band. For the valence band, however, the degeneracy of heavy- and light-hole bands causes band mixing in many semiconductors. This point will be discussed later.)

In such a case, a single-electron eigenstate,

$$\hat{\mathcal{H}}|e\eta\rangle = \varepsilon_{e\eta}|e\eta\rangle, \quad (4.2.26)$$

which is labeled by some set of quantum numbers  $\eta$ , takes the following form:

$$|e\eta\rangle = \int_V d^3r \varphi_{c\eta}(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r})|g\rangle = \int_V d^3r \varphi_{c\eta}(\mathbf{r}) \hat{\psi}_e^\dagger(\mathbf{r})|g\rangle, \quad (4.2.27)$$

$$\varphi_{c\eta}(\mathbf{r}) = \sum_{\mathbf{k}}' \tilde{F}_{c\eta}(\mathbf{k}) \phi_{c\mathbf{k}}(\mathbf{r}) = \sqrt{v_0} \sum_{\ell} F_{c\eta}(\mathbf{R}_\ell) w_c(\mathbf{r} - \mathbf{R}_\ell), \quad (4.2.28)$$

where

$$F_{c\eta}(\mathbf{r}) \equiv \frac{1}{\sqrt{V}} \sum_{\mathbf{k}}' e^{i\mathbf{k}\cdot\mathbf{r}} \tilde{F}_{c\eta}(\mathbf{k}). \quad (4.2.29)$$

The probability amplitude of finding an electron at the position  $\mathbf{r}$  in the subspace which is spanned by  $\phi_{c\mathbf{k}}(\mathbf{r})$ 's is evaluated as

$$\langle g|\hat{\psi}_e(\mathbf{r})|e\eta\rangle = \varphi_{c\eta}(\mathbf{r}). \quad (4.2.30)$$

Therefore, we can interpret  $\varphi_{c\eta}(\mathbf{r})$  as the single-body wavefunction of the electron in the subspace. It is normalized as

$$1 = \langle e\eta|e\eta\rangle = \int_V d^3r |\varphi_{c\eta}(\mathbf{r})|^2 = \sum_{\mathbf{k}}' |\tilde{F}_{c\eta}(\mathbf{k})|^2 = v_0 \sum_{\ell} |F_{c\eta}(\mathbf{R}_\ell)|^2 = \int_V d^3r |F_{c\eta}(\mathbf{r})|^2 \quad (4.2.31)$$

In a similar manner, a single-hole eigenstate takes the following form:

$$\hat{\mathcal{H}}|h\eta\rangle = \varepsilon_{h\eta}|h\eta\rangle \quad (4.2.32)$$

$$|h\eta\rangle = \int_V d^3r \varphi_{v\eta}^*(\mathbf{r}) \hat{\psi}(\mathbf{r})|g\rangle = \int_V d^3r \varphi_{v\eta}^*(\mathbf{r}) \hat{\psi}_h^\dagger(\mathbf{r})|g\rangle, \quad (4.2.33)$$

$$\varphi_{v\eta}(\mathbf{r}) = \sum_{\mathbf{k}}' \tilde{F}_{v\eta}(\mathbf{k}) \phi_{v\mathbf{k}}(\mathbf{r}) = \sqrt{v_0} \sum_{\ell} F_{v\eta}(\mathbf{R}_\ell) w_v(\mathbf{r} - \mathbf{R}_\ell), \quad (4.2.34)$$

$$F_{v\eta}(\mathbf{r}) \equiv \frac{1}{\sqrt{V}} \sum_{\mathbf{k}}' e^{i\mathbf{k}\cdot\mathbf{r}} \tilde{F}_{v\eta}(\mathbf{k}), \quad (4.2.35)$$

where  $\bar{\eta}$  is the “hole-conjugate” of  $\eta$ . That is, we define  $\bar{\eta}$  in such a way that it can be naturally interpreted as a set of quantum numbers of the hole: for a hydrogen-like state, for example,  $\eta = (n, \ell, m, \sigma)$ , where  $(n, \ell, m)$  are the orbital quantum numbers and  $\sigma$  denotes spin, we then take  $\bar{\eta} = (n, \ell, -m, -\sigma)$ . The probability amplitude of finding a hole at the position  $\mathbf{r}$  in the subspace which is spanned by  $\phi_{v\mathbf{k}}(\mathbf{r})$ ’s is given by

$$\langle g | \hat{\psi}_h(\mathbf{r}) | h\eta \rangle = \varphi_{v\bar{\eta}}^*(\mathbf{r}). \quad (4.2.36)$$

Therefore, we can interpret  $\varphi_{v\bar{\eta}}^*(\mathbf{r})$  as the single-body wavefunction of the hole which has the set of quantum numbers  $\bar{\eta}$ . It is normalized as

$$1 = \langle h\eta | h\eta \rangle = \int_V d^3r |\varphi_{v\eta}(\mathbf{r})|^2 = \sum_{\mathbf{k}}' |\tilde{F}_{v\eta}(\mathbf{k})|^2 = v_0 \sum_{\ell} |F_{v\eta}(\mathbf{R}_{\ell})|^2 = \int_V d^3r |F_{v\eta}(\mathbf{r})|^2 \quad (4.2.37)$$

Under our assumptions (i) and (ii),  $F_{b\eta}(\mathbf{r})$  ( $b = c, v$ ) becomes a slowly varying function of  $\mathbf{r}$ , and hence called the “envelope function.” We note that if a function  $A(\mathbf{r})$  is slowly varying and if a function  $B(\mathbf{r})$  is a cell-periodic function, then

$$\int_V d^3r A(\mathbf{r})B(\mathbf{r}) \simeq \sum_{\ell} A(\mathbf{R}_{\ell}) \int_{v_0} d^3\boldsymbol{\rho} B(\boldsymbol{\rho}) \simeq \left[ \int_V d^3r A(\mathbf{r}) \right] \cdot \left[ \frac{1}{v_0} \int_{v_0} d^3\boldsymbol{\rho} B(\boldsymbol{\rho}) \right], \quad (4.2.38)$$

where  $\int_{v_0} d^3\boldsymbol{\rho}$  means the integral over a unit cell. Using this relation and the assumptions (i) and (ii), we can derive the approximate eigenvalue equations for the envelope functions as

$$[\varepsilon_c(-i\nabla) + V_1(\mathbf{r})] F_{c\eta}(\mathbf{r}) = \varepsilon_{c\eta} F_{c\eta}(\mathbf{r}), \quad (4.2.39)$$

$$[-\varepsilon_v(-i\nabla) - V_1(\mathbf{r})] F_{v\eta}(\mathbf{r}) = \varepsilon_{h\bar{\eta}} F_{v\eta}(\mathbf{r}). \quad (4.2.40)$$

In particular, when the bands have parabolic dispersions;

$$\varepsilon_c(\mathbf{k}) = \varepsilon_c(\mathbf{0}) + \frac{\hbar^2 k^2}{2m_e}, \quad (4.2.41)$$

$$\varepsilon_v(\mathbf{k}) = \varepsilon_v(\mathbf{0}) - \frac{\hbar^2 k^2}{2m_h}, \quad (4.2.42)$$

then we obtain the “Schrödinger equations” for the envelope functions:

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + \varepsilon_c(\mathbf{0}) + V_1(\mathbf{r}) \right] F_{c\eta}(\mathbf{r}) = \varepsilon_{c\eta} F_{c\eta}(\mathbf{r}), \quad (4.2.43)$$

$$\left[ -\frac{\hbar^2}{2m_h} \nabla^2 - \varepsilon_v(\mathbf{0}) - V_1(\mathbf{r}) \right] F_{v\eta}(\mathbf{r}) = \varepsilon_{h\bar{\eta}} F_{v\eta}(\mathbf{r}). \quad (4.2.44)$$

These eigenvalue equations are much easier to solve than the original Schrödinger equations (4.2.26) and (4.2.32), because the complicated “crystal potential” in  $\mathcal{H}_{mf}$  are absorbed in the effective masses  $m_e$ ,  $m_h$  and the bottom and top energies of the bands,  $\varepsilon_c(\mathbf{0})$  and  $\varepsilon_v(\mathbf{0})$ , respectively. Once the envelope functions are thus

obtained, the wavefunctions can be obtained from (4.2.28) or (4.2.33). Because of this simplicity, the Schrödinger eqs. for the envelope functions are widely used in the studies of nanostructures. However, care should be taken in discussions of optical properties, as we will explain in the subsequent subsections.

We next consider a state in which an electron-hole pair is excited. In this case we must take account of the strong electron-hole interaction. If the band mixing caused by the interaction is negligible a pair state (exciton state), which is labeled by a set of quantum numbers  $\eta$ , can be written as

$$|x\eta\rangle = \int_V d^3r_e \int_V d^3r_h \varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h) \hat{\psi}_e^\dagger(\mathbf{r}_e) \hat{\psi}_h^\dagger(\mathbf{r}_h) |g\rangle, \quad (4.2.45)$$

$$\varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{\mathbf{k}_e} \sum_{\mathbf{k}_h}' \tilde{F}_{x\eta}(\mathbf{k}_e, \mathbf{k}_h) \phi_{c\mathbf{k}_e}(\mathbf{r}_e) \phi_{v\mathbf{k}_h}^*(\mathbf{r}_h) \quad (4.2.46)$$

$$= v_0 \sum_j \sum_\ell F_{x\eta}(\mathbf{R}_j, \mathbf{R}_\ell) w_c(\mathbf{r}_e - \mathbf{R}_j) w_v^*(\mathbf{r}_h - \mathbf{R}_\ell), \quad (4.2.47)$$

where

$$F_{x\eta}(\mathbf{r}_e, \mathbf{r}_h) = \frac{1}{V} \sum_{\mathbf{k}_e} \sum_{\mathbf{k}_h}' e^{i\mathbf{k}_e \cdot \mathbf{r}_e - i\mathbf{k}_h \cdot \mathbf{r}_h} \tilde{F}_{x\eta}(\mathbf{k}_e, \mathbf{k}_h). \quad (4.2.48)$$

The probability amplitude of finding an electron at the position  $\mathbf{r}_e$  and a hole at  $\mathbf{r}_h$  is evaluated as

$$\langle g | \hat{\psi}_h(\mathbf{r}_h) \hat{\psi}_e(\mathbf{r}_e) | \varphi_{x\eta} \rangle = \varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h). \quad (4.2.49)$$

Therefore,  $\varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h)$  can be interpreted as the wavefunction of the pair. It is normalized as

$$\begin{aligned} 1 &= \langle x\eta | x\eta \rangle = \int_V d^3r_e \int_V d^3r_h |\varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h)|^2 = \sum_{\mathbf{k}_e} \sum_{\mathbf{k}_h}' |\tilde{F}_{x\eta}(\mathbf{k}_e, \mathbf{k}_h)|^2 \\ &= v_0^2 \sum_j \sum_\ell |F_{x\eta}(\mathbf{R}_j, \mathbf{R}_\ell)|^2 = \int_V d^3r_e \int_V d^3r_h |F_{x\eta}(\mathbf{r}_e, \mathbf{r}_h)|^2. \end{aligned} \quad (4.2.50)$$

Note that  $\varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h)$  is not required to be antisymmetric under interchange of  $\mathbf{r}_e$  and  $\mathbf{r}_h$ . That is, we can treat an electron and a hole as if they were different particles (as far as we can neglect the band mixing).

The forms (4.2.46)-(4.2.47) of the wavefunction can describe both the Wannier exciton (for which the effective Bohr radius  $a_B^* \gg$  lattice constant  $a$ ) and the Frenkel exciton (for which  $a_B^* \sim a$ ). We here consider the case of the Wannier exciton, and assume, for simplicity, the parabolic dispersions (4.2.41)-(4.2.42). Then, in a perfect crystal, the total crystal momentum  $\mathbf{K}$  of the pair becomes a good quantum number, and we write  $\eta = (\mathbf{K}, \nu)$ , where  $\nu$  denotes the set of the other quantum numbers. Considering that  $\mathbf{K}$  should be shared between the electron and hole in proportion to their masses, we can take  $\tilde{F}_{x\eta}$  in the following form:

$$\tilde{F}_{x\eta}(\mathbf{k}_e, \mathbf{k}_h) = \sum_{\mathbf{k}}' \tilde{U}_\nu(\mathbf{k}) \delta_{\mathbf{k}_e, \mathbf{k} + \frac{m_e}{M} \mathbf{K}} \delta_{\mathbf{k}_h, \mathbf{k} - \frac{m_h}{M} \mathbf{K}} \equiv \tilde{F}_{\mathbf{K}\nu}(\mathbf{k}_e, \mathbf{k}_h), \quad (4.2.51)$$

where  $\tilde{U}_\nu$  is a function to be determined, and  $M \equiv m_e + m_h$ . Inserting this form into Eq. (4.2.48), we obtain

$$F_{x\eta}(\mathbf{r}_e, \mathbf{r}_h) = \frac{1}{\sqrt{V}} \exp[i\mathbf{K} \cdot \mathbf{R}] U_\nu(\mathbf{r}_e - \mathbf{r}_h) \equiv F_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h) \quad (4.2.52)$$

where we have introduced the center-of-mass coordinate,

$$\mathbf{R} \equiv \frac{m_e \mathbf{r}_e + m_h \mathbf{r}_h}{M}, \quad (4.2.53)$$

and

$$U_\nu(\mathbf{r}) \equiv \frac{1}{\sqrt{V}} \sum_{\mathbf{k}}' e^{i\mathbf{k} \cdot \mathbf{r}} \tilde{U}_\nu(\mathbf{k}). \quad (4.2.54)$$

We can interpret Eq. (4.2.52) as the product of the center-of-mass envelope function  $e^{i\mathbf{K} \cdot \mathbf{R}}/\sqrt{V}$  and the relative-motion envelope function  $U_\nu$ . From (4.2.50) we see that each of them are normalized to 1:

$$1 = \int_V d^3R \left| \frac{1}{\sqrt{V}} \exp[i\mathbf{K} \cdot \mathbf{R}] \right|^2 = \int_V d^3r |U_\nu(\mathbf{r})|^2 = \sum_{\mathbf{k}}' |\tilde{U}_\nu(\mathbf{k})|^2. \quad (4.2.55)$$

The functional form of  $U_\nu$  depends crucially on the electron-hole interaction. The form of the e-h interaction was reviewed, for example, in [1]. It was shown there that the form is nontrivial for  $r \lesssim a_B^*$  because of various exchange potentials and the finite size of the electron and hole. Since we are considering Wannier excitons, the long-range parts of the interactions are more important than the short-range parts. The dominant e-h interaction would then be the screened Coulomb attraction  $-e^2/\epsilon r$ , where  $\epsilon$  is the dielectric constant. When the e-h interaction is approximated by it, the “Schrödinger equation” for  $U_\nu$  takes the familiar form;

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{\epsilon r} \right] U_\nu = E_\nu U_\nu, \quad (4.2.56)$$

where  $\mu$  is the reduced mass,  $1/\mu = 1/m_e + 1/m_h$ . By solving the simple eigenvalue equation (4.2.56), we can calculate the eigen-energy  $E_{\mathbf{K}\nu}$  and the wavefunction  $\varphi_{\mathbf{K}\nu}$  of the state  $|\mathbf{K}\nu\rangle$ . That is,

$$E_{\mathbf{K}\nu} = E_G + E_\nu + \frac{\hbar^2 K^2}{2M}. \quad (4.2.57)$$

We see that the exciton energy consists of the band gap energy  $E_G$ , the energy of the e-h relative motion  $E_\nu$ , and the energy of the center-of-mass motion  $\hbar^2 K^2/2M$ . The binding energy of the e-h pair is  $-E_\nu$ . We can obtain the wavefunction  $\varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h) \equiv \varphi_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h)$  by inserting the eigenfunction  $U_\nu$  into Eq. (4.2.52), and the resulting expression into (4.2.47):

$$\begin{aligned} \varphi_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h) &= v_0 \sum_j \sum_\ell \frac{1}{\sqrt{V}} \exp \left[ i\mathbf{K} \cdot \frac{m_e \mathbf{R}_j + m_h \mathbf{R}_\ell}{M} \right] U_\nu(\mathbf{R}_j - \mathbf{R}_\ell) \\ &\quad \times w_c(\mathbf{r}_e - \mathbf{R}_j) w_v^*(\mathbf{r}_h - \mathbf{R}_\ell). \end{aligned} \quad (4.2.58)$$

Or, we may insert  $\tilde{U}_\nu$  into (4.2.46) to get

$$\varphi_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h) = \frac{1}{\sqrt{V}} \exp[i\mathbf{K} \cdot \mathbf{R}] S_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h), \quad (4.2.59)$$

$$S_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}}' \exp[i\mathbf{k} \cdot (\mathbf{r}_e - \mathbf{r}_h)] \tilde{U}_\nu(\mathbf{k}) u_{c\mathbf{k}+\frac{m_e}{M}\mathbf{K}}(\mathbf{r}_e) u_{v\mathbf{k}-\frac{m_h}{M}\mathbf{K}}^*(\mathbf{r}_h). \quad (4.2.60)$$

Note that we can replace  $u_c(\mathbf{r}_e)$  and  $u_v(\mathbf{r}_h)$  with  $u_c(\boldsymbol{\rho}_e)$  and  $u_v(\boldsymbol{\rho}_h)$ , respectively, where  $\boldsymbol{\rho}_e$  and  $\boldsymbol{\rho}_h$  denote the position vectors which are reduced in a unit cell (i.e., they are  $\mathbf{r}_e$  and  $\mathbf{r}_h$  measured from the center of the unit cells in which  $\mathbf{r}_e$  and  $\mathbf{r}_h$  are located, respectively).

Actually, except for high-quality crystals kept at a low-enough temperature, the crystal momentum  $\mathbf{K}$  of the center-of-mass motion is not conserved because the exciton is scattered by phonons, impurities and/or defects, and the exciton wavefunctions are modified. For example, when the total potential of impurities is slowly-varying (i.e., characteristic length of the variation  $\gg a_B^*$ ) the wavefunction of an exciton state  $|N\nu\rangle$  which is trapped by the impurities may be obtained as superposition of  $\varphi_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h)$  over various  $\mathbf{K}$ 's,

$$\varphi_{N\nu}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{\mathbf{K}}' \tilde{G}_{N\nu}(\mathbf{K}) \varphi_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h) \quad (4.2.61)$$

$$= v_0 \sum_j \sum_\ell G_{N\nu} \left( \frac{m_e \mathbf{R}_j + m_h \mathbf{R}_\ell}{M} \right) U_\nu(\mathbf{R}_j - \mathbf{R}_\ell) \times w_c(\mathbf{r}_e - \mathbf{R}_j) w_v^*(\mathbf{r}_h - \mathbf{R}_\ell), \quad (4.2.62)$$

where  $\tilde{G}_{N\nu}$  is a superposition coefficient, with  $N$  being a quantum number, and

$$G_{N\nu}(\mathbf{R}) \equiv \frac{1}{\sqrt{V}} \sum_{\mathbf{K}}' \tilde{G}_{N\nu}(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{R}} \quad (4.2.63)$$

can be regarded as the envelope function of the trapped center-of-mass motion. It is normalized as

$$\int_V G_{N\nu}^*(\mathbf{R}) G_{N'\nu}(\mathbf{R}) d^3R = \sum_{\mathbf{K}}' \tilde{G}_{N\nu}^*(\mathbf{K}) \tilde{G}_{N'\nu}(\mathbf{K}) = \delta_{N,N'}. \quad (4.2.64)$$

The trapping may be viewed as the Anderson localization of the exciton, where the size  $\ell_G$  of the spatial extension of  $G_{N\nu}(\mathbf{R})$  is the localization length  $\ell_{loc}$ . We may also use the form (4.2.61) or (4.2.62) as an approximate wavefunction when the quantum coherence of the center-of-mass motion is broken by scatterings by phonons or other excitons. In this case  $\ell_G$  is the phase breaking length  $\ell_\phi$ . Both the localization and the phase breaking may be important in real systems, and  $\ell_G$  would be given roughly by

$$\ell_G \simeq \min[\ell_{loc}, \ell_\phi]. \quad (4.2.65)$$

It will be shown later that the oscillator strength of the exciton is proportional to  $\ell_G^3$  when  $\ell_G$  is less than the wavelength of the optical field.

In a similar manner, states with two or more e-h pairs can be written in terms of two- or more-particle wavefunctions as

$$\begin{aligned} & \int_V d^3r_e^1 \int_V d^3r_e^2 \cdots \int_V d^3r_h^1 \int_V d^3r_h^2 \cdots \varphi(\mathbf{r}_e^1, \mathbf{r}_e^2, \dots, \mathbf{r}_h^1, \mathbf{r}_h^2, \dots) \\ & \times \hat{\psi}_e^\dagger(\mathbf{r}_e^1) \hat{\psi}_e^\dagger(\mathbf{r}_e^2) \cdots \hat{\psi}_h^\dagger(\mathbf{r}_h^1) \hat{\psi}_h^\dagger(\mathbf{r}_h^2) \cdots |g\rangle. \end{aligned} \quad (4.2.66)$$

General states are linear combinations and/or classical mixture of such states with zero, one, and more e-h pairs.

### 4.2.3 Optical Matrix Elements

The envelope functions should not be taken as the true wavefunctions because optical phenomena are frequently accompanied with transitions between the cell-periodic parts  $u_{b\mathbf{k}}$ 's of the Bloch functions. That is, optical matrix elements depend not only on the envelope functions but also on the functional forms of  $u_{b\mathbf{k}}$ 's (or, equivalently, of the Wannier functions). The latter dependence becomes crucial when nonlinear optical processes or intraband transitions are discussed. Unfortunately, this point was disregarded in much literature, and unphysical results were sometimes reported. We here present typical matrix elements for the states described in the previous subsection.

The interaction with an external optical field  $\mathbf{A}(\mathbf{r}, t)$  in the Coulomb gauge takes the following form:

$$\hat{\mathcal{H}}_I = \int_V d^3r \hat{\psi}^\dagger(\mathbf{r}) \left[ -\frac{\hbar e}{imc} \mathbf{A} \cdot \nabla + \frac{e^2}{2mc^2} A^2 \right] \hat{\psi}(\mathbf{r}), \quad (4.2.67)$$

$$= \hat{\mathcal{H}}_I^{(1)} + \hat{\mathcal{H}}_I^{(2)}, \quad (4.2.68)$$

where  $\hat{\mathcal{H}}_I^{(1)}$  is linear in  $\mathbf{A}$ , whereas  $\hat{\mathcal{H}}_I^{(2)}$  is quadratic. To evaluate various matrix elements of  $\hat{\mathcal{H}}_I^{(1)}$  and  $\hat{\mathcal{H}}_I^{(2)}$ , it is useful to derive formulas for matrix elements of a general operator of the form

$$\hat{Q} = \int_V d^3r \int_V d^3r' Q(\mathbf{r}, \mathbf{r}') \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}'). \quad (4.2.69)$$

In some cases, its expectation value in the ground state  $|g\rangle$  does not vanish. Such a non-zero expectation value in the ground state can be absorbed by redefinition of the operator. This means a change of the zero of energy when  $\hat{Q}$  is a part of the Hamiltonian. The redefinition is most conveniently accomplished by the “normal order” with respect to  $\hat{\psi}_e$  and  $\hat{\psi}_h$ . The normally-ordered  $\hat{Q}$  is

$$\begin{aligned} : \hat{Q} : &= \int_V d^3r \int_V d^3r' Q(\mathbf{r}, \mathbf{r}') : \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}') : \\ &= \int_V d^3r \int_V d^3r' Q(\mathbf{r}, \mathbf{r}') \left[ \hat{\psi}_e^\dagger(\mathbf{r}) \hat{\psi}_e(\mathbf{r}') + \hat{\psi}_e^\dagger(\mathbf{r}) \hat{\psi}_h^\dagger(\mathbf{r}') \right. \\ &\quad \left. + \hat{\psi}_h(\mathbf{r}) \hat{\psi}_e(\mathbf{r}') - \hat{\psi}_h^\dagger(\mathbf{r}') \hat{\psi}_h(\mathbf{r}) \right], \end{aligned} \quad (4.2.70)$$

which differs from  $\hat{Q}$  only by a c-number term. Using Eq. (4.2.14) and the anti-commutation relations, we can easily show that

$$\langle g | : \hat{Q} : | g \rangle = 0, \quad (4.2.71)$$

$$\langle x\eta | : \hat{Q} : | g \rangle = \int_V d^3 r_1 \int_V d^3 r_2 \varphi_{x\eta}^*(\mathbf{r}_1, \mathbf{r}_2) Q(\mathbf{r}_1, \mathbf{r}_2), \quad (4.2.72)$$

$$\begin{aligned} \langle x\eta | : \hat{Q} : | x\eta' \rangle &= \int_V d^3 r_1 \int_V d^3 r_2 \int_V d^3 r_3 [\varphi_{x\eta}^*(\mathbf{r}_1, \mathbf{r}_3) Q(\mathbf{r}_1, \mathbf{r}_2) \varphi_{x\eta'}(\mathbf{r}_2, \mathbf{r}_3) \\ &\quad - \varphi_{x\eta}^*(\mathbf{r}_3, \mathbf{r}_1) Q(\mathbf{r}_2, \mathbf{r}_1) \varphi_{x\eta'}(\mathbf{r}_3, \mathbf{r}_2)]. \end{aligned} \quad (4.2.73)$$

These formulas enable us to evaluate various matrix elements from the two-body wavefunction  $\varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h)$ .

For an optical field whose photon energy is of the order of  $E_G$  or less, the wavelength  $\lambda$  of  $\mathbf{A}$  is hundreds nano meters or longer. When the spatial extension of  $\varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h)$  is smaller than  $\lambda$  we can approximate matrix elements of  $\mathcal{H}_I$  as

$$\langle x\eta | : \mathcal{H}_I^{(1)} : | g \rangle \simeq -\frac{\hbar e}{imc} \mathbf{A}(\mathbf{r}_{x\eta}) \int_V d^3 r \langle x\eta | : \hat{\psi}^\dagger(\mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla \hat{\psi}(\mathbf{r}) : | g \rangle, \quad (4.2.74)$$

$$\langle x\eta | : \mathcal{H}_I^{(2)} : | g \rangle \simeq \frac{e^2}{2mc^2} A^2(\mathbf{r}_{x\eta}) \int_V d^3 r \langle x\eta | : \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) : | g \rangle, \quad (4.2.75)$$

and similarly for other matrix elements. Here,  $\mathbf{r}_{x\eta}$  denotes the center position around which  $\varphi_{x\eta}$  is localized. We may use, for example,  $\varphi_{N\nu}$  for  $\varphi_{x\eta}$ , and evaluate the above integrals using (4.2.72) by putting  $Q(\mathbf{r}, \mathbf{r}') = \boldsymbol{\epsilon} \cdot \nabla \delta(\mathbf{r} - \mathbf{r}')$  and  $Q(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ , respectively. From Eqs. (4.2.59), (4.2.60) and (4.2.61), we find

$$\int_V d^3 r \langle N\nu | : \hat{\psi}^\dagger(\mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla \hat{\psi}(\mathbf{r}) : | g \rangle = \int_V d^3 r [\boldsymbol{\epsilon} \cdot \nabla' \varphi_{N\nu}^*(\mathbf{r}, \mathbf{r}')]_{\mathbf{r}' \rightarrow \mathbf{r}} \quad (4.2.76)$$

$$= \tilde{G}_{N\nu}(\mathbf{0}) \sum_{\mathbf{k}}' \tilde{U}_\nu^*(\mathbf{k}) (c\mathbf{k} | \boldsymbol{\epsilon} \cdot \nabla | v\mathbf{k}), \quad (4.2.77)$$

$$\int_V d^3 r \langle N\nu | : \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) : | g \rangle = \int_V d^3 r \varphi_{N\nu}^*(\mathbf{r}, \mathbf{r}) = 0, \quad (4.2.78)$$

where we have utilized Eqs. (4.2.3), (4.2.5) and (4.2.38), and

$$(c\mathbf{k} | \boldsymbol{\epsilon} \cdot \nabla | v\mathbf{k}) \equiv \frac{1}{v_0} \int_{v_0} d^3 \rho u_{c\mathbf{k}}^*(\mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla u_{v\mathbf{k}}(\mathbf{r}) \quad (4.2.79)$$

represents contribution from each cell. If this integral is independent of  $\mathbf{k}$  in the range of  $\mathbf{k}$  for which  $\tilde{U}_\nu(\mathbf{k})$  is not small, then we denote the integral by  $(c | \boldsymbol{\epsilon} \cdot \nabla | v)$  and Eq. (4.2.77) is reduced to

$$\int_V d^3 r \langle N\nu | : \hat{\psi}^\dagger(\mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla \hat{\psi}(\mathbf{r}) : | g \rangle = \sqrt{V} \tilde{G}_{N\nu}^*(\mathbf{0}) U_\nu^*(\mathbf{0}) (c | \boldsymbol{\epsilon} \cdot \nabla | v) \quad (4.2.80)$$

At first sight this result might look unphysical because of the anomalous factor  $\sqrt{V}$ . However, this factor is canceled by the factor  $1/\sqrt{V}$  in  $\tilde{G}_{N\nu}(\mathbf{0})$ . This can be seen as follows. Recall that we have assumed that the exciton state is well localized,  $\ell_G < \lambda$ . For  $\varphi_{N\nu}$  to be well localized  $\tilde{G}_{N\nu}(\mathbf{K})$  must be a smooth function of  $\mathbf{K}$ , and we can replace the summation in Eq. (4.2.64) with the integral as

$$1 = \sum_{\mathbf{K}}' |\tilde{G}_{N\nu}(\mathbf{K})|^2 = \frac{V}{(2\pi)^3} \int d^3K |\tilde{G}_{N\nu}(\mathbf{K})|^2 \quad (4.2.81)$$

Considering also that the spatial extension of  $G_{N\nu}$  is of the order of  $\ell_G$ , we find that the maximum value of  $|\tilde{G}_{N\nu}(\mathbf{0})|$  should behave as

$$\max_N |\tilde{G}_{N\nu}(\mathbf{0})| \sim \sqrt{\frac{V_G}{V}} \quad (4.2.82)$$

where we have put, apart from an unimportant numerical factor of order unity,

$$V_G \sim \ell_G^3 \quad (4.2.83)$$

Therefore, the matrix element (4.2.80) is independent of  $V$ , as it should be. The matrix element is actually proportional to  $\sqrt{V_G}$ , which is sometimes called the “coherence volume” [4] [5] because it gives a measure of the volume of the space region over which the exciton wavefunction is coherent. An important consequence of the  $V_G$  dependence of the matrix element is that the radiative recombination rate  $\Gamma_{N\nu}^{\text{rad}}$  of the exciton is proportional to  $V_G$  in the region where  $\ell_G < \lambda$  [4] [5]. According to Eq. (4.2.65), this phenomenon may be observed in quantum wells and in quantum dots, as the dependence of  $\Gamma_{N\nu}^{\text{rad}}$  on temperature (on which  $\ell_\phi$  depends) and on the dot size ( $\simeq \ell_{\text{loc}}$ ), respectively. The size dependence of  $\Gamma_{N\nu}^{\text{rad}}$  of quantum dots was clearly observed by Nakamura et al. [6] and Itoh et al. [7], whereas the temperature dependence of  $\Gamma_{N\nu}^{\text{rad}}$  of quantum wells reported by Feldmann et al. [4] could be interpreted as due to the temperature dependence of the exciton distribution because the experiment was performed at relatively high temperatures [8].

Note that the result (4.2.80) can also be obtained when we neglect the  $\mathbf{k}$  dependence of  $u_c$  and  $u_v^*$  in Eq. (4.2.59) as

$$S_{\mathbf{K}\nu}(\mathbf{r}_e, \mathbf{r}_h) \simeq U_\nu(\mathbf{r}_e - \mathbf{r}_h) u_{c0}(\mathbf{r}_e) u_{v0}^*(\mathbf{r}_h) \equiv S_\nu^{(0)}. \quad (\text{often wrong}) \quad (4.2.84)$$

In this approximation, the wavefunction  $\varphi_{N\nu}$ , for example, is decoupled into the envelope function of the center-of-mass motion, that of relative motion, and cell-periodic parts as

$$\varphi_{N\nu}(\mathbf{r}_e, \mathbf{r}_h) \simeq G_{N\nu}(\mathbf{R}) U_\nu(\mathbf{r}_e - \mathbf{r}_h) u_{c0}(\mathbf{r}_e) u_{v0}^*(\mathbf{r}_h) \equiv \varphi_{N\nu}^{(0)}(\mathbf{r}_e, \mathbf{r}_h). \quad (\text{often wrong}) \quad (4.2.85)$$

This approximation has been used in much literature because of its simplicity. This approximation is sometimes good for simple cases such as the band-to-band matrix element between direct-allowed bands which are non-degenerate. In studies of nonlinear optical phenomena, however, we must also evaluate other matrix

elements. For such general matrix elements, *the approximate forms (4.2.84) and (4.2.85) often give wrong and unphysical results*, as we now explain.

As a typical example let us investigate the transition matrix elements between different exciton states. When the spatial extension of both the initial and final states are smaller than  $\lambda$ , we find from formula (4.2.73)

$$\langle x\eta | : \mathcal{H}_I^{(1)} : | x\eta' \rangle \simeq -\frac{\hbar e}{imc} \mathbf{A}(\mathbf{r}_{x\eta}) \int_V d^3 r_e \int_V d^3 r_h \varphi_{x\eta}^*(\mathbf{r}_e, \mathbf{r}_h) \boldsymbol{\epsilon} \cdot (\nabla_e + \nabla_h) \varphi_{x\eta'}(\mathbf{r}_e, \mathbf{r}_h). \quad (4.2.86)$$

Here, you can arbitrarily replace  $\mathbf{A}(\mathbf{r}_{x\eta})$  with  $\mathbf{A}(\mathbf{r}_{x\eta'})$ , because  $\mathbf{A}(\mathbf{r}_{x\eta}) \simeq \mathbf{A}(\mathbf{r}_{x\eta'})$  from our assumption  $\lambda < \ell_G$ . The point is that derivatives of *both* the envelope functions and cell-periodic parts contribute to this matrix element. For the latter, we can use the group-velocity formula;

$$\int_V d^3 r \phi_{b\mathbf{k}}^*(\mathbf{r}) \frac{\hbar}{im} \nabla \phi_{b\mathbf{k}}(\mathbf{r}) = \frac{1}{\hbar} \frac{\partial \varepsilon_b(\mathbf{k})}{\partial \mathbf{k}}, \quad (b = c, v) \quad (4.2.87)$$

where  $m$  denotes the free-electron mass. For the parabolic dispersion (4.2.41)-(4.2.42), this yields

$$(c\mathbf{k}|\nabla|c\mathbf{k}) = i \left( \frac{m}{m_e} - 1 \right) \mathbf{k}, \quad (4.2.88)$$

$$(v\mathbf{k}|\nabla|v\mathbf{k}) = i \left( -\frac{m}{m_h} - 1 \right) \mathbf{k}. \quad (4.2.89)$$

It is seen that the derivatives of the cell-periodic parts can never be neglected unless  $m_e = m$  and  $m_h = -m$ . For example, when  $m_e \simeq m_h \simeq m$  the derivatives are  $(c\mathbf{k}|\nabla|c\mathbf{k}) \simeq 0$  and  $(v\mathbf{k}|\nabla|v\mathbf{k}) \simeq -2i\mathbf{k}$ . Physically, these derivatives represent modification of velocities (whose operator is  $\hbar\nabla/im$  in the absence of electromagnetic fields) due to Bragg reflections by the crystal potential. The modification is larger for holes than for electrons because usually both  $m_e$  and  $m_h$  are positive. Use of the simplified forms (4.2.84) or (4.2.85) leads to the total neglect of these derivatives (because they vanish at  $\mathbf{k} = \mathbf{0}$ ), and often results in unphysical results. For example, when  $\varphi_{x\eta} = \varphi_{N\nu}$  we find

$$\begin{aligned} \langle N\nu | : \mathcal{H}_I^{(1)} : | N'\nu' \rangle &\simeq -\frac{\hbar e}{imc} \mathbf{A}(\mathbf{r}_{x\eta}) \left[ \delta_{\nu,\nu'} \int_V d^3 R G_{N\nu}^*(\mathbf{R}) \boldsymbol{\epsilon} \cdot \nabla G_{N'\nu}(\mathbf{R}) \right. \\ &\quad \left. + \frac{m}{\mu} \int_V d^3 R G_{N\nu}^*(\mathbf{R}) G_{N'\nu'}(\mathbf{R}) \int_V d^3 r U_\nu^*(\mathbf{r}) \boldsymbol{\epsilon} \cdot \nabla U_{\nu'}(\mathbf{r}) \right]. \end{aligned} \quad (4.2.90)$$

Note that the first and second terms of the right hand side (rhs) become finite for different values of  $N, \nu, N'$  and  $\nu'$ . Note also that the typical value of the first term is much smaller than that of the second term because  $a_B^* \ll \ell_G$  (by our assumption on  $\varphi_{N\nu}$ ) and  $\mu < m$  (e.g.,  $m/\mu \sim 10$  for GaAs). On the other hand, if we took  $\varphi_{x\eta} = \varphi_{N\nu}^{(0)}$  we could obtain the first term only;

$$\langle N\nu^{(0)} | : \mathcal{H}_I^{(1)} : | N'\nu'^{(0)} \rangle \simeq -\frac{\hbar e}{imc} \mathbf{A}(\mathbf{r}_{x\eta}) \delta_{\nu,\nu'} \int_V d^3 R G_{N\nu}^*(\mathbf{R}) \boldsymbol{\epsilon} \cdot \nabla G_{N'\nu}(\mathbf{R}). \quad (4.2.91)$$

It is clear that the use of the simplified form  $\varphi_{N\nu}^{(0)}$  would lead to wrong results for the matrix element, *both in magnitude and in the selection rules*. Therefore, we cannot use the simplified forms (4.2.84) and (4.2.85) for physical processes in which exciton scatterings by optical fields are involved. Such processes include, for example, second-order nonlinear responses and third-order processes in which the exciton scatterings by optical fields are involved as intermediate (virtual) states.

It seems worthwhile to point out another difficulty arising from the use of the simplified forms. Equations (4.2.88) and (4.2.89) suggest that  $u_{b\mathbf{k}}$ 's play important roles in the gauge invariance of the theory. However, the use of the simplified forms is equivalent to the fixing of  $u_{b\mathbf{k}}$ 's on  $u_{b\mathbf{0}}$ 's which are defined in some particular gauge. As a result, *the gauge invariance of such a theory is violated*,<sup>2</sup> and physical predictions of the theory depend on the gauge [10] [11]. No definite conclusions can be drawn from such a theory, of course.

Both of the above difficulties become severer if one proceeds from linear optical processes to nonlinear processes. Unfortunately, however, the simplified forms (4.2.84) and (4.2.85) have been used in much literature which discusses nonlinear optical processes, without any consideration on these difficulties. The most appropriate way of calculation is to use the correct wavefunctions (4.2.60) and (4.2.61) together with the original interaction Hamiltonian (4.2.68). There are alternative ways in which one may use the simplified form (4.2.85). One way is to use of the "length formula" for the interaction [9] [10]:

$$\hat{\mathcal{H}}_I^{length} = e \int_V d^3r \hat{\psi}^\dagger(\mathbf{r}) \mathbf{r} \cdot \mathbf{E} \hat{\psi}(\mathbf{r}). \quad (4.2.92)$$

This expression is rather anomalous because the value of  $\mathbf{r}$  extends to infinity as  $V \rightarrow \infty$ . Therefore, the normally-order form  $:\hat{\mathcal{H}}_I^{length}:$  should be used in actual calculations. It is not difficult to show that this interaction together with the simplified form (4.2.85) give the correct results. The other way is to perform calculation according to the following prescription: In calculations of the *envelope functions* and matrix elements of *intraband transitions* (exciton-exciton scatterings), use the following Luttinger-Kohn Hamiltonian as an effective "intraband Hamiltonian" for the envelope function  $G_{N\nu}U_\nu$  [10];

$$H_{intra}^{env} \equiv \frac{1}{2m_e} \left( \frac{\hbar}{i} \nabla_e + \frac{e}{c} \mathbf{A} \right)^2 + \frac{1}{2m_h} \left( \frac{\hbar}{i} \nabla_h - \frac{e}{c} \mathbf{A} \right)^2 - \frac{e^2}{\epsilon |\mathbf{r}_e - \mathbf{r}_h|}. \quad (4.2.93)$$

In calculations of matrix elements of *interband transitions* (exciton creation and annihilation), on the other hand, one must use the bare interaction  $\hat{\mathcal{H}}_I$ . Physically, this prescription indicates that slowly-varying phenomena are determined by the effective masses whereas the rapidly-varying phenomena are determined by the free-electron mass [1].

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<sup>2</sup> There is another possible origin of the violation of the gauge invariance of the theory. It is some nonlocal interaction, such as the exchange interaction, which may appear as a result of a mean-field approximation [9]. In our case, however, such an interaction has been neglected because we are considering Wannier excitons.

#### 4.2.4 Quantum States in Nanostructures

The above formulation must be modified to treat nanostructures, such as quantum wells (QWs) and quantum wires (QWRs), because the band structures are modified by the quantum confinement, and also because nanostructures are usually made of semiconductors which have degenerate valence bands (whereas we have assumed for simplicity that the bands are non-degenerate). One way to take account of these effects is to combine the  $\mathbf{k} \cdot \mathbf{p}$  theory with the exciton theory, which would enable us to determine (though perturbatively) both the band structure and the exciton wavefunction simultaneously.

We here describe another simpler way — a rigid-band approximation. This approximation may be valid (i) in the case where the quantum confinement is very strong (i.e., the confinement energy  $\gg$  the exciton binding energy) and also (ii) in the case where the quantum confinement is very weak (i.e., the confinement energy  $\ll$  the exciton binding energy) *and* both the  $c$  and  $v$  bands are non-degenerate (i.e., these bands are energetically separated around  $\mathbf{k} = \mathbf{0}$  from other bands, and the energy separation is larger than the exciton binding energy). We can take the band structures as those of the nanostructure and the bulk crystal for cases (i) and (ii), respectively, because the band structure would be rigid against the e-h interaction. The electron and hole operators can be defined according to the rigid band structure. We can then evaluate exciton states taking the e-h interaction into account. Using these exciton states, we can evaluate various optical properties, such as nonlinear susceptibilities, of the nanostructure.

In case (ii), in particular, the rigid bands are the bands of *the bulk crystal*, and the only important effect of the quantum confinement would be the confinement of the center-of-mass motion. Hence we may employ  $\varphi_{N\nu}$  of (4.2.61) as the exciton wavefunction, and the formulations of the previous subsections can be applied directly. A typical example is the 1s exciton in a quantum dot whose size is larger than  $a_B^*$  and which is made of non-degenerate semiconductors. For higher energy states (2p, 3d, and so on), the weak-confinement assumption becomes worse because the spatial extension of the e-h relative motion becomes larger for higher energies.

In case (i), on the other hand, the band structure would be modified by the quantum confinement, but the *modified* band structure would *not* be affected strongly by the e-h interaction. In GaAs/AlGaAs nanostructures, for example, the two-fold degeneracy at the top of the valence bands is lifted by the quantum confinement, and two series of subbands are formed, which are called the heavy-hole subbands and light-hole subbands. The subbands are no longer degenerate at the top of the valence bands. By the assumption that the intersubband energy separation is larger than the exciton binding energy, the e-h interaction would not alter the subband structure strongly. In this case, we may take the single-body eigenstates of the mean-field Hamiltonian *of the nanostructure* as basis functions. For concreteness, we assume for a nanostructure a quantum well structure of well width  $L$  and area  $S$ , and  $a \ll L \ll a_B^*$  ( $a$  is the lattice constant). The cases of a quantum wire and quantum dot can be formulated in similar manners. Then, a single-body eigenstate (of low energies) may be approximated by the following

form;

$$\phi_{bn\mathbf{k}_{\parallel}}(\mathbf{r}) = \sqrt{\frac{v_0}{S}} \sum_{\ell} \exp[i\mathbf{k}_{\parallel} \cdot \mathbf{R}_{\ell\parallel}] F_{bn}(Z_{\ell}) w_b(\mathbf{r} - \mathbf{R}_{\ell}; \mathbf{R}_{\ell}), \quad (4.2.94)$$

where  $n$  denotes a quantum number,  $\mathbf{k}_{\parallel}$  and  $\mathbf{R}_{\ell\parallel}$  denote two-dimensional vectors which represent the wavenumber and the cell position, respectively, in the QW plane (xy plane), and  $Z_{\ell}$  is the  $z$  coordinate of the cell position, i.e.,  $\mathbf{R}_{\ell} = (\mathbf{R}_{\ell\parallel}, Z_{\ell})$ . Note that  $b$  here labels the bands which are modified (the degeneracy is lifted) by the quantum confinement, and  $w_b(\mathbf{r} - \mathbf{R}_{\ell}; \mathbf{R}_{\ell})$  denotes the Wannier function of the *modified band* in the well (when  $\mathbf{R}_{\ell} \in$  well region) or barrier (when  $\mathbf{R}_{\ell} \in$  barrier region). The Wannier functions and the envelope function  $F_{bn}$  may be obtained, e.g., by using the  $\mathbf{k} \cdot \mathbf{p}$  perturbations. In particular, for bands which are non-degenerate in the bulk crystal, we may approximate  $w_b$  by that of the bulk crystal, and  $F_{bn}$  may be obtained by solving the effective-mass equation;

$$\varepsilon_b \left( \mathbf{k}_{\parallel}, -i \frac{\partial}{\partial z}; z \right) F_{bn\mathbf{k}_{\parallel}}(z) = \varepsilon_{bn\mathbf{k}_{\parallel}} F_{bn\mathbf{k}_{\parallel}}(z), \quad (4.2.95)$$

where  $\varepsilon_b(\mathbf{k}_{\parallel}, k_z; z)$  is the dispersion of the bulk band of the semiconductor which composes the well (when  $z \in$  well region) or barrier (when  $z \in$  barrier region). For a parabolic band, in particular, Eq. (4.2.95) becomes

$$\left[ \frac{\hbar^2 k_{\parallel}^2}{2m_{b\parallel}(z)} - \frac{\hbar^2}{2m_{bz}(z)} \frac{\partial^2}{\partial z^2} + \varepsilon_b(\mathbf{0}; z) \right] F_{bn\mathbf{k}_{\parallel}}(z) = \varepsilon_{bn\mathbf{k}_{\parallel}} F_{bn\mathbf{k}_{\parallel}}(z). \quad (4.2.96)$$

Here we have considered the fact that in general the effective mass  $m_b$  becomes anisotropic by the band mixing. The  $\mathbf{k}_{\parallel} \rightarrow \mathbf{0}$  limit of this equation is the familiar form;

$$\left[ -\frac{\hbar^2}{2m_{bz}(z)} \frac{\partial^2}{\partial z^2} + \varepsilon_b(\mathbf{0}; z) \right] F_{bn}(z) = \varepsilon_{bn} F_{bn}(z), \quad (4.2.97)$$

where  $F_{bn} \equiv F_{bn\mathbf{0}}$  and  $\varepsilon_{bn} \equiv \varepsilon_{bn\mathbf{0}}$ . Equations (4.2.96) and (4.2.97) are basically particle-in-a-box problems. Note however that the boundary conditions on  $F_{bn\mathbf{k}}$  or  $F_{bn}$  at heterojunctions depend on the functional forms of  $w_b(\mathbf{r} - \mathbf{R}_{\ell}; \mathbf{R}_{\ell})$ . For example, when  $w_b$  takes different values across a heterojunction (because the semiconductors are different on both sides) then  $F_{bn\mathbf{k}}$  must be discontinuous in order for the wavefunction to be continuous across the heterojunction [12].

For a typical GaAs/AlGaAs QW, the conduction band is non-degenerate and we may use Eq. (4.2.95), whereas the valence bands are degenerate and we should use another method such as the  $\mathbf{k} \cdot \mathbf{p}$  perturbation. However, Eqs. (4.2.95)-(4.2.97) have been widely used even for the valence bands. This may be justified if we replace  $w_b$  with that of the QW (i.e.,  $w_b$  which is evaluated with the  $\mathbf{k} \cdot \mathbf{p}$  perturbation) and simultaneously adjust parameters in  $\varepsilon_b(\mathbf{k}_{\parallel}, k_z; z)$  of Eq. (4.2.95) in such a way that the wavefunction agrees with the result of the  $\mathbf{k} \cdot \mathbf{p}$  perturbation.

We can also construct the wavefunction of an exciton, using the Wannier functions of the QW, as

$$\varphi_{x\eta}(\mathbf{r}_e, \mathbf{r}_h) = v_0 \sum_j \sum_{\ell} F_{x\eta}(\mathbf{R}_j, \mathbf{R}_{\ell}) w_c(\mathbf{r}_e - \mathbf{R}_j; \mathbf{R}_j) w_v^*(\mathbf{r}_h - \mathbf{R}_{\ell}; \mathbf{R}_{\ell}). \quad (4.2.98)$$

The envelope function  $F_{x\eta}(\mathbf{r}_e, \mathbf{r}_h)$  can be evaluated from, say, an effective-mass equation. Using  $\varphi_{x\eta}$ 's thus obtained, we can evaluate various optical matrix elements in a similar manner to the previous subsections. The most important point in this case is that the Wannier functions (and therefore the cell periodic functions) become anisotropic when the band degeneracy is lifted by the quantum confinement [13]. For example, when the valence band degeneracy is lifted, the matrix elements between the cell periodic functions become anisotropic, and, for small  $k$ ,

$$(v\mathbf{k}|\nabla|v\mathbf{k}) = i \left( -\frac{m}{m_h(\hat{\mathbf{k}})} - 1 \right) \mathbf{k}, \quad (4.2.99)$$

where  $\hat{\mathbf{k}}$  denotes the unit vector which is parallel to  $\mathbf{k}$ . The interband matrix element also becomes anisotropic, which for small  $k$  we denote as

$$\lim_{\mathbf{k} \rightarrow 0} (c\mathbf{k}|\boldsymbol{\epsilon} \cdot \nabla|v\mathbf{k}) = (c|\boldsymbol{\epsilon} \cdot \nabla|v\hat{\mathbf{k}}). \quad (4.2.100)$$

These anisotropies of the cell-periodic parts have been observed as anisotropies of various optical properties of QWs. It is clear that as is the case of the bulk crystal (subsection 4.2.3) optical matrix elements must be evaluated carefully.

We have calculated in Refs. [14] [15] [16] [17] [18] linear as well as nonlinear optical properties of nanostructures using the above formulation. Up to now some of the results have been confirmed experimentally [20] [19] [21].

#### 4.2.5 Quantum Optical Phenomena in Nanostructures

So far the photon field has been treated as a classical field. In recent years, however, quantum optical phenomena in nanostructures have been studied by many researchers. We here depict some examples from our work.

The first example is the quantum nondemolition measurement of the photon number using an electron interferometer which is composed of double quantum wires [22] [23]. It was shown that one can measure the photon number of a quantum state of photons using the electron interferometer as a photodetector in such a way that the post-measurement state of the photons carries the same information on the photon number as the pre-measurement state. When the pre-measurement state is an eigenstate of the photon number, in particular, the wavefunction is unchanged by the measurement, whereas the observer obtains information on the photon number. In contrast, when the observer uses conventional photodetector the information on the photon number is lost by the measurement: when he uses a photodiode, for example, the post-measurement photon state is the zero-photon state, which has no information on the pre-measurement state. In Refs.[22] [23] various quantities, such as the density operator of the post measurement state and the measurement error, have been calculated as a function of the pre-measurement state of the quantized photon field and the structural parameters of the quantum-wire interferometer.

The second example is the photon creation from a false vacuum of semiconductors [24]. In quantum field theory, particles are created when a parameter(s) in the Lagrangian (or, equivalently, in the field equations) have time dependence even if

the initial state is the vacuum state (which is defined before the time variation begins) [25]. Since this is a general property, we can expect such phenomena also in condensed matter. For example, photons may be created if a material parameter(s) varies as a function of time [26] [27]. We have pointed out that conventional discussions on the photon creation in condensed matter, which are based on phenomenological quantization of the macroscopic photon field, break down near the exciton resonance [24]. To treat the exciton resonance correctly, we have proposed the use of a two-field model, in which both the photon field and the exciton field is taken into account as microscopic degrees of freedom [24]. The two-field model has allowed us to evaluate the creation spectra over a wide energy range. It is also pointed out there that even a slight singularity in the functional form of the time variation of the parameters causes large deviation from non-singular (physical) results, whereas singular forms were assumed in much literature.

The third example is the radiative lifetime of an excited atom in an inhomogeneous and absorptive cavity [28]. We have demonstrated strong dependence of the lifetime on the material parameters such as the absorption coefficient and the cavity structure. The forth example is the photon statistics of light emitting diodes (LEDs) at a low injection level [29]. We have derived a formula which gives the photon statistics as a function of the pump statistics, device parameters, and the detection efficiency of each photon mode.

These are only a very limited examples of the quantum optical phenomena in nanostructures. More examples will be presented in the subsequent sections and in the references cited therein.

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